The *H*-theorem in the Boltzmann approximation for association and dissociation reactions for the case of quantum internal states of molecules

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The results of the author's earlier paper [Sov. Phys. JETP **71**, 690 (1990)] are generalized to the case where the internal states of molecules are quantum variables while the coordinates and momenta of the molecules' centers of mass are quasiclassical. It is assumed that $v^{1/3}\Delta P \gg \hbar$, where $v = V/N$, and $\Delta P = \langle P^2\rangle^{1/2}$ is the rms spread of momenta, and that $v^{1/6} r_{\rm int}^{1/2}\Delta P \gg \hbar$. The former condition makes it possible to ignore exchange effects (the case of weak degeneracy).

1. INTRODUCTION

In Ref. 1 the *H*-theorem was proved in the Boltzmann approximation for the association and dissociation reactions $A + B \rightleftarrows C$ and $A + B + C \rightleftarrows D$ of complex molecules, that is, molecules with internal degrees of freedom. There the setting was totally classical. The natural approach is to generalize the theory to include the quantum case, and the first step is to consider the quantum internal states of molecules. The discussion will be restricted to the reactions of the $A + B \rightleftarrows C$ type; $A + B + C \rightleftarrows D$ reactions can be considered in a similar manner. The reader will recall (see Ref. 1) that for $A + B \rightleftarrows C$ reactions at least one of the molecules, A or B, must be complex; otherwise the reactions do not take place because two conservation laws, of momentum and of energy, must be satisfied simultaneously. When both A and B are simple, a third body M is required and the reactions proceed according to the scheme $A + B + M \rightleftarrows C + M$.

When the molecules are structureless, that is, possess no internal degrees of freedom or these are not taken into account, the quantum Boltzmann equation has the form (see, e.g., Refs. 2–4)

$$f_j(\mathbf{r},\mathbf{p}_j) = -\frac{\mathbf{p}_j}{m_j}\nabla_r f_j + 2\pi\sum_l\int [f_j' f_l'(1+\vartheta_j f_j)(1+\vartheta_l f_l) - f_j f_l(1+\vartheta_j f_j')(1+\vartheta_l f_l')]\,\alpha(v_{jl},\chi)\sin\chi\, d\chi\, d\mathbf{p}_l. \quad (1.1)$$

where $\vartheta_j = (2\pi\hbar)^3\delta_j/G_j$ is the statistical weight of the molecule of the jth species, with $\delta_j = -1$ and $\delta_j = 1$ for the Fermi–Dirac and the Bose–Einstein statistics, respectively; $\alpha(v_{jl},\chi)$ the scattering cross section; and χ the angle of deflection of the trajectory when molecules of the jth and lth species interact.

The normalization of the distribution functions in Eq. (1.1) and in what follows is the one accepted in Ref. 3, where $\int f_j d^3\mathbf{p}_j$ is the number of particles of the jth species per unit volume.

The addition of $\vartheta_j f_j$ to unity in Eq. (1.1) is due to exchange effects (symmetry effects). These manifest themselves weakly when

$$v_j^{1/3}\Delta p_j \gg \hbar, \quad (1.2)$$

for any value of j, with $v_j = V/N_j$ and $\Delta p_j = \langle p_j^2\rangle^{1/2}$. Condition (1.2) is met even for light molecules of gases, except at extremely low temperatures. Therefore, we ignore exchange effects.

The discrepancy between the expression $\alpha(v_{jl},\chi)\sin\chi d\chi$ in Eq. (1.1) and the classical expression $v_{jl} b db$ is due to quantum diffraction effects in molecular collisions. These effects are small when $r_{\rm int}\Delta p \gg \hbar$, where $r_{\rm int}$ is the interaction radius of the molecules. We assume that $r_{\rm int}\Delta p \sim \hbar$ (or even $r_{\rm int}\Delta p \ll \hbar$, but $r_{\rm int}^{1/2} v^{1/6}\Delta p \gg \hbar$), that is, diffraction effects do take place. The method employed in the present approach makes it possible not to introduce diffraction explicitly.

For association and dissociation to occur, at least a fraction of the molecules must be complex, that is, must possess internal degrees of freedom. As in Ref. 1, we denote the coordinates and momenta of the mass centers of molecules by $\mathbf{r}_j$ and $\mathbf{P}_j$, respectively, with j standing for the species of the molecules. The set of internal coordinates $\mathbf{q}_{j2}',\dots,\mathbf{q}_{jk_j}'$, defined in formula (2.1) of Ref. 1, is designated q_j, and the set $\mathbf{p}_{j2}',\dots,\mathbf{p}_{jk_j}'$, defined in formula (2.2) of Ref. 1, is designated p_j. Then, for the quantum case, instead of the classical distribution function $f_j(\mathbf{r}_j,\mathbf{P}_j,q_j,p_j)$ we must introduce an operator $\hat{F}_j$ with the following matrix elements:

$$F_j(\mathbf{r}_j, q_j, \mathbf{r}_j', q_j') = \langle \mathbf{r}_j, q_j|\hat{F}_j|\mathbf{r}_j', q_j'\rangle$$

(the coordinate representation). We assume, however, that the state of the mass center of the molecules is quasiclassical in view of the condition $\Delta r_j\Delta P_j = V^{1/3}\Delta P_j \gg \hbar$ or, in other words, the state of the molecules is quasiclassical in $\mathbf{r}_j$ and $\mathbf{P}_j$. Then the state of the molecules is characterized by an operator function $\hat{f}_j(\mathbf{r}_j,\mathbf{P}_j)$ with the following matrix elements:

$$f_j(\mathbf{r}_j, \mathbf{P}_j, q_j, q_j') = \langle q_j|\hat{f}_j(\mathbf{r}_j, \mathbf{P}_j)|q_j'\rangle, \quad (1.2a)$$

that is, $\hat{f}_j$ is a function of $\mathbf{r}_j$ and $\mathbf{P}_j$ and an operator of the other variables. As in Ref. 1, we take the variables $\mathbf{r}_{12}$, q_1, and q_2, with $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, for the internal coordinates q_3 of molecule C. The total Hamiltonians of molecules $A = E_1$, $B = E_2$, and $C = E_3$ are sums of external and internal Hamiltonians:

$$\hat{H}_j = (2M_j)^{-1}\hat{P}_j^2 + \hat{H}_j^{in},$$

where the Hamiltonian of the center of mass is assumed nonquantum. On the other hand, calculations show that the Hamiltonian $\hat{H}_j^{\rm in}$ is expressed only in terms of the operators of the internal coordinates and momenta:

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$$\hat{H}_j^{in}=\sum_{\tau=2}^{k_j}(2m_\tau^{(j)})^{-1}(\hat{p}_{j\tau}')^2+(2m_1^{(j)})^{-1}\Big(\sum_{\tau=2}^{k_j}\hat{p}_{j\tau}'\Big)^2+U_j(\hat{q}_j).$$

Specifically, when $q_3=(\mathbf{r}_{12},q_1,q_2)$, we have

$$\hat{H}_3^{in}=\hat{H}_1^{in}+\hat{H}_2^{in}+{}^1/_2(M_1^{-1}+M_2^{-1})\hat{P}_{12}^2+\Phi(\hat{\mathbf{r}}_{12},\ \hat{q}_1,\ \hat{q}_2).\quad(1.3)$$

where $\hat{\mathbf{P}}_{12}=(M_2/M_3)\hat{\mathbf{P}}_1-(M_1/M_3)\hat{\mathbf{P}}_2=-i\hbar\partial/\partial\mathbf{r}_{12}\equiv-i\hbar\nabla_{12}$, and Φ is the potential energy of the interaction of molecules A and B. Since $M_3^{-1}\hat{\mathbf{P}}_3^2+(M_1^{-1}+M_2^{-1})\hat{\mathbf{P}}_{12}^2=M_1^{-1}\hat{\mathbf{P}}_1^2+M_2^{-1}\hat{\mathbf{P}}_2^2$, the kinetic energy entering into $\hat{H}_3$, where we must allow for (1.3), is equal to the sum of the kinetic energies entering into $\hat{H}_1$ and $\hat{H}_2$, which is corroborated by (1.3). And because $r_{\text{int}}\Delta P\lesssim\hbar$, the internal state of the molecules is quantum rather than classical.

We select a quantity r_0 that satisfies the inequalities

$$r_{\text{int}}\ll r_0\ll v^{1/3},\quad r_0\Delta P\gg\hbar.\qquad(1.4)$$

When $r_0=r_{\text{int}}^{1/2}v^{1/6}$, the inequality $r_0\Delta P\gg\hbar$ follows from the inequality $r_{\text{int}}^{1/2}v^{1/6}\Delta P\gg\hbar$. We assume, for the time being, that molecules A and B merge into molecule C when $r_{12}<r_0$, that is, when $\mathbf{r}_{12}$ belongs to a ball D of radius r_0, and do not merge if this condition is not met. Within (1.4) the exact choice of r_0 is unimportant. If we bring into the picture the region

$$r_0/2\leqslant r_{12}\leqslant 3r_0/2,\qquad(1.5)$$

which includes the surface σ of D, the transient state of molecule C in this region is quasiclassical in the variables $\mathbf{r}_{12}$ and $\mathbf{P}_{12}$ because of the condition $r_0\Delta P\gg\hbar$. It is this fact that underlies the considerations that follow.

2. ENTROPY OF MOLECULES OF DIFFERING SPECIES

As is known, the quantum entropy of structureless particles of each species is given by (see, e.g., Ref. 5)

$$S_j=-k\int d\mathbf{r}\,d\mathbf{p}\Big[f_j(\mathbf{r},\mathbf{p})\ln\Big(\frac{|\vartheta_j|f_j}{1+\vartheta_jf_j}\Big)-\frac{1}{\vartheta_j}\ln(1+\vartheta_jf_j)\Big],\qquad(2.1)$$

where ϑ_j has the same meaning as in (1.1). The expression in the square brackets can be represented as follows:

$$f_j\ln(|\vartheta_j|f_j)-f_j-\frac{1}{2}\vartheta_jf_j^2+\ldots=f_j\ln(|\vartheta_j|f_j)-f_j\Big[1+O\Big(\frac{\hbar^3}{v\Delta p^3}\Big)\Big].$$

Hence, if condition (1.2) is met we can employ instead of Eq. (2.1), with sufficient accuracy,

$$S_j=-k\int d\mathbf{r}\,d\mathbf{p}\,f_j(\mathbf{r},\mathbf{p})[\ln(|\vartheta_j|f_j)-1].$$

Allowing for the complexity of the molecules, we must replace $f_j(r,\mathbf{p})$ with the operator function $\hat{f}_j(\mathbf{r},\mathbf{P}_j)$. In the spatially homogeneous case we have

$$s_j=\frac{S_j}{V}=-k\,\mathrm{Tr}_j\int d\mathbf{P}_j\hat{f}_j(\mathbf{P}_j)[\ln(\gamma_j\hat{f}_j)-\hat{I}],\qquad(2.2)$$

with $\gamma_j=|\vartheta_j|=(2\pi\hbar)^3/G_j$, $\hat{I}$ the identity operator, and Tr_j the trace over the internal variables of a molecule of the jth species. The formula constitutes a direct generalization of Eq. (4.5) in Ref. 1 to the case of quantum internal states and refers to molecules A and B, that is, in it $j=1,2$.

In writing the entropy density $s_3=S_3/V$ of molecule C we must bear in mind that by convention C exists only when $|\mathbf{r}_{12}|\leqslant r_0$. Clearly, the number of molecules C per unit volume is

$$n_3=\int d\mathbf{P}_3\mathrm{Tr}_1\mathrm{Tr}_2\int_D d\mathbf{r}_{12}\hat{f}_3|_{r_{12}'=r_{12}}=\int d\mathbf{P}_3\,dq_1\,dq_2\int_D d\mathbf{r}_{12}\times f_3(\mathbf{P}_3,\mathbf{r}_{12},q_1,q_2,\mathbf{r}_{12},q_1,q_2).\qquad(2.3)$$

Similarly, the entropy density is not

$$s_3=\mathrm{Tr}_3\int d\mathbf{P}_3\hat{G}_3=\int d\mathbf{P}_3\mathrm{Tr}_1\mathrm{Tr}_2\iiint_{-\infty}^{\infty}d\mathbf{r}_{12}G_3|_{\mathbf{r}_{12}'=\mathbf{r}_{12}},$$

but

$$s_3=\int d\mathbf{P}_3\mathrm{Tr}_1\mathrm{Tr}_2\int_D d\mathbf{r}_{12}\hat{G}_3|_{\mathbf{r}_{12}'=\mathbf{r}_{12}}\equiv\int d\mathbf{P}_3\,dq_1\,dq_2\int_D d\mathbf{r}_{12}\times g_3(\mathbf{P}_3,\mathbf{r}_{12},q_1,q_2,\mathbf{r}_{12},q_1,q_2),\qquad(2.4)$$

where

$$\hat{G}_3=-k\hat{f}_3(\mathbf{P}_3)\{\ln[\gamma_3\hat{f}_3(\mathbf{P}_3)]-\hat{I}\},$$

$$g_3(\mathbf{P}_3,\mathbf{r}_{12},q_1,q_2,\mathbf{r}_{12}',q_1',q_2')=\langle\mathbf{r}_{12},q_1,q_2|\hat{G}_3(\mathbf{P}_3)|\mathbf{r}_{12}',q_1',q_2'\rangle.$$

Differentiating Eq. (2.4) with respect to time and allowing for (1.2a) and (1.3), we find that

$$(\dot{s}_3)_{as}+(\dot{s}_3)_{dis}=-\frac{i}{\hbar}\int d\mathbf{P}_3\mathrm{Tr}_1\mathrm{Tr}_2\int_D d\mathbf{r}_{12}[\hat{H}_3^{in},\hat{G}_3]_{r_{12}'=r_{12}}=-\frac{i}{\hbar}\int d\mathbf{P}_3\mathrm{Tr}_1\mathrm{Tr}_2\int_D d\mathbf{r}_{12}\Big[\frac{1}{2M_0}\hat{P}_{12}^2,\hat{G}_3\Big]_{r_{12}'=r_{12}},\qquad(2.5)$$

where we have introduced the notation $M_0^{-1}=M_1^{-1}+M_2^{-1}$ and employed the fact that $\mathrm{Tr}_1[\hat{H}_1^{\text{in}},\hat{G}_3]=0$, $\mathrm{Tr}_2[\hat{H}_2^{\text{in}},\hat{G}_3]=0$, and $\mathrm{Tr}_1\mathrm{Tr}_2[\hat{\Phi},\hat{G}_3]_{\mathbf{r}_{12}=\mathbf{r}_{12}}=0$, since in the coordinate representation $\hat{\Phi}=\Phi(\hat{r}_{12},\hat{q}_1,\hat{q}_2)$ is diagonal. Indeed, the matrix elements of $[\hat{\Phi},\hat{G}_3]$ are

$$g_3(\mathbf{r}_{12},q_1,q_2,\mathbf{r}_{12}',q_1',q_2')[\Phi(\mathbf{r}_{12},q_1,q_2)-\Phi(\mathbf{r}_{12}',q_1',q_2')],$$

which vanish if we put $\mathbf{r}'_{12} = \mathbf{r}_{12}$, $q'_1 = q_1$, and $q'_2 = q_2$.

Since $\widehat{\mathbf{P}}_{12} = -i\hbar\nabla_{12}$, we can write Eq. (2.5) as

$(\dot{s}_{3\mathrm{as}} + (\dot{s}_3)_{\mathrm{dis}}$

$$(\dot{s}_3)_{as}+(\dot{s}_3)_{dis} = \frac{i\hbar}{2M_0}\int d\mathbf{P}_3\,\mathrm{Tr}_1\,\mathrm{Tr}_2\int_D d\mathbf{r}_{12}[\nabla_{12}^2, \hat{G}_3]_{\mathbf{r}_{12}'=\mathbf{r}_{12}}. \tag{2.6}$$

The operator $\hat{\varphi}(\mathbf{P}_3,\mathbf{r}_{12},\mathbf{P}_{12})$ with matrix elements $\varphi(\mathbf{P}_3,\mathbf{r}_{12},\mathbf{P}_{12},q_1,q_2,q'_1,q'_2)$ is defined as the result of a partial Wigner transformation:

$$\begin{aligned}\varphi(\mathbf{P}_3,\ldots,q_2')=(2\pi\hbar)^{-3}\int \exp(-i\hbar^{-1}\mathbf{P}_{12}\mathbf{s})\,\cdot\\ \cdot g_3\left(\mathbf{P}_3, \mathbf{r}_{12}+\frac{\mathbf{s}}{2}, q_1, q_2, \mathbf{r}_{12}-\frac{\mathbf{s}}{2}, q_1', q_2'\right) d\mathbf{s}.\end{aligned} \tag{2.7}$$

We denote this transformation by $\mathscr{W}_0$, that is,

$$\hat{\varphi}=\mathscr{W}_0\{\hat{G}_3\}=-k\mathscr{W}_0\{\hat{f}_3[\ln(\gamma_3\hat{f}_3)-\hat{I}]\}.$$

The inverse of transformation (2.7) is

$$\begin{aligned}&g_3(\mathbf{P}_3, \mathbf{r}_{12}, \mathbf{r}_{12}')\\ &=\int \exp[i\hbar^{-1}\mathbf{P}_{12}(\mathbf{r}_{12}-\mathbf{r}_{12}')]\varphi\left(\mathbf{P}_3, \frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2}, \mathbf{P}_{12}\right) d\mathbf{P}_{12},\end{aligned} \tag{2.8}$$

with q_1,q_2,q'_1, and q'_2 not written explicitly. We use (2.8) to transform the commutator $[\nabla^2_{12},\hat{G}_3]$, where $\nabla_{12}\hat{G}_3$ stands for the derivative $\partial g_3/\partial\mathbf{r}_{12}$ and $\hat{G}_3\nabla_{12}$ for $-\partial g_3/\partial\mathbf{r}'_{12}$. It is easy to verify that for any function u we have

$$\begin{aligned}&\left[\left(\frac{\partial}{\partial\mathbf{r}_{12}}\right)^2-\left(\frac{\partial}{\partial\mathbf{r}_{12}'}\right)^2\right]u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2}, \mathbf{r}_{12}-\mathbf{r}_{12}'\right)\\ &\qquad=2\nabla_1\nabla_2 u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2}, \mathbf{r}_{12}-\mathbf{r}_{12}'\right),\end{aligned}$$

where ∇_1 and ∇_2 are the del operators referring to the first and second vector arguments of function u, respectively.

Applying this equality to Eq. (2.8) yields

$$\begin{aligned}&\left[\left(\frac{\partial}{\partial\mathbf{r}_{12}}\right)^2-\left(\frac{\partial}{\partial\mathbf{r}_{12}'}\right)^2\right]g_3\\ &=\frac{2i}{\hbar}\int \exp[i\hbar^{-1}\mathbf{P}_{12}(\mathbf{r}_{12}-\mathbf{r}_{12}')]\mathbf{P}_{12}\frac{\partial}{\partial\mathbf{R}}\varphi(\mathbf{P}_3, \mathbf{R}, \mathbf{P}_{12})d\mathbf{P}_{12}\end{aligned}$$

at $\mathbf{R} = (\mathbf{r}_{12} + \mathbf{r}'_{12})/2$. Hence,

$$[\nabla_{12}^2, \hat{G}_3]_{\mathbf{r}_{12}'=\mathbf{r}_{12}} = \frac{2i}{\hbar}\nabla_{12}\int \mathbf{P}_{12}\varphi(\mathbf{P}_3, \mathbf{r}_{12}, \mathbf{P}_{12})d\mathbf{P}_{12}. \tag{2.9}$$

Substituting (2.9) into (2.6) and transforming the integral over the region D into an integral over the surface σ via the divergence theorem, we arrive at

$$\begin{aligned}&(\dot{s}_3)_{as}+(\dot{s}_3)_{dis}\\ &=k\,\mathrm{Tr}_1\,\mathrm{Tr}_2\int d\mathbf{P}_3\,d\mathbf{P}_{12}\int_\sigma d\sigma(\mathbf{v}_{12})_\nu\mathscr{W}_0\{\hat{f}_3[\ln(\gamma_3\hat{f}_3)-\hat{I}]\},\end{aligned} \tag{2.10}$$

where ν is the unit outward normal at $d\sigma$, $(\mathbf{v}_{12})_\nu = \nu\cdot\mathbf{v}_{12}$, and $\mathbf{v}_{12} = \mathbf{P}_{12}/M_0 = \mathbf{P}_1/M_1 - \mathbf{P}_2/M_2$.

Up to this point all reasoning that led to (2.10) was exact. Now we employ the approximate equality

$$\mathscr{W}_0\{\hat{f}_3[\ln(\gamma_3\hat{f}_3)-\hat{I}]\}\approx\mathscr{W}_0[\hat{f}_3]\{\ln\{(2\pi\hbar)^3\gamma_3\mathscr{W}_0[\hat{f}_3]\}-1\}, \tag{2.11}$$

valid on σ. This relation, as shown in Appendix A, is caused by the inequalities $r_0 \gg r_{\mathrm{int}}$ and $r_0\Delta P \gg \hbar$. It follows essentially from the fact that the transient quantum state in the region specified by (1.5) is quasiclassical in $\mathbf{r}_{12}$ and $\mathbf{P}_{12}$.

If we introduce the notation $\mathscr{W}_0[\hat{f}_3(\mathbf{P}_3)] = \hat{F}_3(\mathbf{P}_3,\mathbf{r}_{12},\mathbf{P}_{12})$, then, in view of (2.11), Eq. (2.10) assumes the form

$$\begin{aligned}(\dot{s}_3)_{as}+(\dot{s})_{dis}=k\,\mathrm{Tr}_1\,\mathrm{Tr}_2\int d\mathbf{P}_3\,d\mathbf{P}_{12}\int_\sigma d\sigma(\mathbf{v}_{12})_\nu\hat{F}_3\\ \times\{\ln[(2\pi\hbar)^3\gamma_3\hat{F}_3]-\hat{I}\},\end{aligned} \tag{2.12}$$

which is the quantum generalization of formula (5.6) in Ref. 1.

3. VARIOUS CONTRIBUTIONS TO THE DERIVATIVE OF THE ENTROPY DENSITY

We partition the sphere σ into the entrance hemisphere σ_-, where $\mathbf{r}_{12}\cdot\mathbf{v}_{12} < 0$, that is, $(\mathbf{v}_{12})_\nu < 0$, and the exit hemisphere σ_+, where $(\mathbf{v}_{12})_\nu \geqslant 0$. Then the integral in Eq. (2.12) consists of two parts:

$$(\dot{s}_3)_{as}=k\,\mathrm{Tr}_1\,\mathrm{Tr}_2\int d\mathbf{P}_3\,d\mathbf{P}_{12}\int_{\sigma_-} d\sigma_-(\mathbf{v}_{12})_\nu\hat{F}_3\{\ln[(2\pi\hbar)^3\hat{F}_3]-1\}, \tag{3.1}$$

$$(\dot{s}_3)_{dis}=k\,\mathrm{Tr}_1\,\mathrm{Tr}_2\int d\mathbf{P}_3\,d\mathbf{P}_{12}\int_{\sigma_+} d\sigma_+(\mathbf{v}_{12})_\nu\hat{F}_3\{\ln[(2\pi\hbar)^3\hat{F}_3]-1\}. \tag{3.2}$$

When the trajectory $r_{12}(t)$ (the notion of a trajectory can be used because the transient quantum state in the region specified by (1.5) is quasiclassical in $\mathbf{r}_{12}$ and $\mathbf{P}_{12}$) intersects the entrance hemisphere, formally molecules A and B transform instantly into molecule C. Since prior to this transformation A did not interact with B, the operator $\hat{F}_3$ on σ_- is a product of $\hat{f}_1$ and $\hat{f}_2$:

$$\hat{F}_3(\mathbf{P}_3, \mathbf{r}_{12}, \mathbf{P}_{12})=\hat{f}_1\left(\frac{M_1}{M_3}\mathbf{P}_3+\mathbf{P}_{12}\right)\hat{f}_2\left(\frac{M_2}{M_3}\mathbf{P}_3-\mathbf{P}_{12}\right), \quad \mathbf{r}_{12}\in\sigma_-. \tag{3.3}$$

The reader will recall that exchange effects are not taken into account here. The operators $\hat{f}_1 = \hat{f}'_1 \otimes \hat{I}''$ and $\hat{f}_2 = \hat{I}' \otimes \hat{f}''_2$ entering into (3.3) commute. Here $\hat{I}'$ and $\hat{I}''$ are identity operators, $\hat{f}'_1$ and $\hat{I}'$ act on the wave functions from the Hilbert space of the first molecule, and $\hat{f}''_2$ and $\hat{I}''$ on the wave functions from the Hilbert space of the second molecule. Substitution of (3.3) into (3.1) yields

$$(\dot{s}_3)_{as}=k\,\mathrm{Tr}_1\mathrm{Tr}_2\int d\mathbf{P}_1\,d\mathbf{P}_2\int_{\sigma_-} d\sigma_-(\mathbf{v}_{12})_\nu\hat{f}_1\hat{f}_2[\ln(\gamma_1\gamma_2\hat{f}_1\hat{f}_2)-\hat{I}]. \tag{3.4}$$

where we have allowed for the fact that $(2\pi\hbar)^3\gamma_3 = \gamma_1\gamma_2$ because $G_3 = G_1G_2$ and replaced the integration variables via the relation $d^3P_3d^3P_{12} = dP_1d^3P_2$.

Turning our attention to the exit hemisphere, we introduce the notation

$$\hat{F}_3(\mathbf{P}_3, \mathbf{r}_{12}, \mathbf{P}_{12}) = \hat{F}_3'\left(\frac{M_1}{M_3}\mathbf{P}_3+\mathbf{P}_{12}, \frac{M_2}{M_3}\mathbf{P}_3-\mathbf{P}_{12}, \mathbf{r}_{12}\right).$$

Allowing for this and replacing the integration variables $\mathbf{P}_3$ and $\mathbf{P}_{12}$ with $\mathbf{P}_1$ and $\mathbf{P}_2$, we can write (3.2) as

$$(\dot{s}_3)_{dis} = k\,\mathrm{Tr}_1\,\mathrm{Tr}_2 \int d\mathbf{P}_1\,d\mathbf{P}_2 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \hat{F}_3' \times (\mathbf{P}_1, \mathbf{P}_2, \mathbf{r}_{12})\,[\ln(\gamma_1\gamma_2\hat{F}_3') - \hat{I}]. \tag{3.5}$$

The reasoning that has led from (2.4) to (3.4) and (3.5) can be applied to any concrete realization of operator $\hat{G}_3$, including $\hat{G}_3 = \hat{f}_3$. Hence, differentiating (2.3) with respect to time, we arrive in a similar manner at

$$\dot{n}_3 = (\dot{n}_3)_{as} + (\dot{n}_3)_{dis}, \quad (\dot{n}_3)_{as} = -\mathrm{Tr}_1\,\mathrm{Tr}_2 \int d\mathbf{P}_1\,d\mathbf{P}_2 \int_{\sigma_-} d\sigma_- (\mathbf{v}_{12})_\nu \hat{f}_1\hat{f}_2,$$

$$(\dot{n}_3)_{dis} = -\mathrm{Tr}_1\,\mathrm{Tr}_2 \int d\mathbf{P}_1\,d\mathbf{P}_2 \int d\sigma_+ (\mathbf{v}_{12})_\nu \hat{F}_3'.$$

We see that

$$\mathrm{Tr}_1\,\mathrm{Tr}_2\,\Delta\mathbf{P}_3\Delta\mathbf{P}_{12}\Delta\sigma_+(\mathbf{v}_{12})_\nu\hat{F}_3(\mathbf{P}_3, \mathbf{r}_{12}, \mathbf{P}_{12}) = \mathrm{Tr}_1\,\mathrm{Tr}_2\,\Delta\mathbf{P}_1\Delta\mathbf{P}_2\Delta\sigma_+(\mathbf{v}_{12})_\nu\hat{F}_3'(\mathbf{P}_1, \mathbf{P}_2, \mathbf{r}_{12})$$

can be interpreted as the number of C molecule per unit volume with momenta in the $\Delta\mathbf{P}_3\Delta\mathbf{P}_{12}$ range that disintegrate per unit time because of the passage of trajectory $r_{12}(t)$ through the surface area element $\Delta\sigma_+$, that is, due to dissociation. This is also the number of pairs of A and B molecules with momenta in the $\Delta\mathbf{P}_1\Delta\mathbf{P}_2$ range that emerge per unit volume per unit time thanks to this process. It is easy to see that the derivatives $(\dot{\hat{f}}_1)_{\rm dis}$ and $(\dot{\hat{f}}_2)_{\rm dis}$ caused by dissociation are:

$$\dot{\hat{f}}_1(\mathbf{P}_1)_{dis} = \mathrm{Tr}_2 \int d\mathbf{P}_2 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \hat{F}_3'(\mathbf{P}_1, \mathbf{P}_2, \mathbf{r}_{12}),$$

$$\dot{\hat{f}}_2(\mathbf{P}_2)_{dis} = \mathrm{Tr}_1 \int d\mathbf{P}_1 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \hat{F}_3'(\mathbf{P}_1, \mathbf{P}_2, \mathbf{r}_{12}). \tag{3.6}$$

In a similar manner, by allowing for (3.3), we arrive at formulas for the derivatives caused by association:

$$\dot{\hat{f}}_1(\mathbf{P}_1)_{as} = \mathrm{Tr}_2 \int d\mathbf{P}_2 \int_{\sigma_-} d\sigma_- (\mathbf{v}_{12})_\nu \hat{f}_1(\mathbf{P}_1)\hat{f}_2(\mathbf{P}_2),$$

$$\dot{\hat{f}}_2(\mathbf{P}_2)_{as} = \mathrm{Tr}_1 \int d\mathbf{P}_1 \int d\sigma_- (\mathbf{v}_{12})_\nu \hat{f}_1(\mathbf{P}_1)\hat{f}_2(\mathbf{P}_2). \tag{3.7}$$

Since $\hat{f}_1$ and $\hat{f}_2$ are independent of $\mathbf{r}_{12}$, we have

$$\int_{\sigma_-} d\sigma_- (\mathbf{v}_{12})_\nu \hat{f}_1\hat{f}_2 = \hat{f}_1\hat{f}_2 \int_{\sigma_-} d\sigma_- \mathbf{v}\mathbf{v}_{12}.$$

But

$$\int_{\sigma_-} d\sigma_- \mathbf{v}\mathbf{v}_{12} = -|\mathbf{v}_{12}|\pi r_0^2 = -\int_{\sigma_+} d\sigma_+ \mathbf{v}\mathbf{v}_{12}. \tag{3.8}$$

We can therefore write (3.7) as follows

$$\dot{\hat{f}}_1(\mathbf{P}_1)_{as} = -\mathrm{Tr}_2 \int d\mathbf{P}_2 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \hat{f}_1\hat{f}_2,$$

$$\dot{\hat{f}}_2(\mathbf{P}_2)_{as} = -\mathrm{Tr}_1 \int d\mathbf{P}_1 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \hat{f}_1\hat{f}_2. \tag{3.9}$$

Similarly, employing (3.8), we can transform Eq. (3.4) into

$$(\dot{s}_3)_{as} = -k\,\mathrm{Tr}_1\,\mathrm{Tr}_2 \int d\mathbf{P}_1\,d\mathbf{P}_2 \int d\sigma_+ (\mathbf{v}_{12})_\nu \hat{f}_1\hat{f}_2 \tag{3.10}$$

Differentiating the entropy densities (2.2) with respect to time and combining the result with (3.6) and (3.9), we get

$$(\dot{s}_1)_{as} + (\dot{s}_1)_{dis} = k\,\mathrm{Tr}_1\,\mathrm{Tr}_2 \int d\mathbf{P}_1\,d\mathbf{P}_2 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \times \ln(\gamma_1\hat{f}_1)(\hat{f}_1\hat{f}_2 - \hat{F}_3')$$

and similarly for $(\dot{s}_2)_{\rm as} + (\dot{s}_2)_{\rm dis}$. Summing $(\dot{s}_1)_{\rm as} + (\dot{s}_1)_{\rm dis}$ and $(\dot{s}_2)_{\rm as} + (\dot{s}_2)_{\rm dis}$ yields

$$(\dot{s}_1+\dot{s}_2)_{as} + (\dot{s}_1+\dot{s}_2)_{dis} = k\,\mathrm{Tr}_1\,\mathrm{Tr}_2 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \ln(\gamma_1\gamma_2\hat{f}_1\hat{f}_2)(\hat{f}_1\hat{f}_2 - \hat{F}_3'). \tag{3.11}$$

It only remains to add the contributions (3.5), (3.10), and (3.11) to obtain the final result:

$$\dot{s}_{as} + \dot{s}_{dis} = \frac{k}{\gamma_1\gamma_2} \int d\mathbf{P}_1\,d\mathbf{P}_2 \int_{\sigma_+} d\sigma_+ (\mathbf{v}_{12})_\nu \times \mathrm{Tr}_1\,\mathrm{Tr}_2[\gamma_1\gamma_2\hat{F}_3' \ln(\gamma_1\gamma_2\hat{F}_3') - \gamma_1\gamma_2\hat{F}_3' + \gamma_1\gamma_2\hat{f}_1\hat{f}_2 - \gamma_1\gamma_2\hat{F}_3' \ln(\gamma_1\gamma_2\hat{f}_1\hat{f}_2)].$$

Allowing for the fact that $(\mathbf{v}_{12})_\nu > 0$ on σ_+ and, as shown in Appendix B, that

$$\mathrm{Tr}(\hat{A}\ln\hat{A} - \hat{A} + \hat{B} - \hat{A}\ln\hat{B}) \geqslant 0 \tag{3.12}$$

which is an operator inequality valid for any Hermitian nonnegative definite matrix $\hat{A}$ and any Hermitian positive definite matrix B, we arrive at the sought result $\dot{s}_{\rm as} + \dot{s}_{\rm dis} \geqslant 0$. Obviously, in (3.12) we must put $\hat{A} = \gamma_1\gamma_2\hat{F}_3'$ and $\hat{B} = \gamma_1\gamma_2\hat{f}_1\hat{f}_2$.

4. CONCLUDING REMARKS

A similar method of proving the *H*-theorem for the case of quantum internal states can be applied to reactions of the A + B + C ⇄ D type and also to more complex reactions of association and dissociation. For the process in which three molecules are associated into one and for the reverse process it is expedient to define the range of bound states by the inequality $\rho_{01}^2 \leqslant r_0^2$, that is, $r_{21}^2 + r_{31}^2 \leqslant r_0^2$ (see Ref. 1). Here the analog of (2.5) is

$$(\dot{s}_4)_{as}+(\dot{s}_4)_{dis}=-\frac{i}{2\hbar}\int d\mathbf{P}_4\,\mathrm{Tr}_1\,\mathrm{Tr}_2\,\mathrm{Tr}_3\int_D d\boldsymbol{\rho}_{01}\left[\sum_{\mu\nu}M_{\mu\nu}{}^{-1}\hat{\mathbf{P}}_{\mu1}\hat{\mathbf{P}}_{\nu1},\hat{G}_4\right]_{\rho_{01}'=\rho_{01}}$$

where

$$\sum_{\mu\nu}M_{\mu\nu}{}^{-1}\hat{\mathbf{P}}_{\mu1}\hat{\mathbf{P}}_{\nu1}=M_2{}^{-1}\hat{P}_{21}{}^2+M_3{}^{-1}\hat{P}_{31}{}^2+M_1{}^{-1}(\hat{\mathbf{P}}_{21}+\hat{\mathbf{P}}_{31})^2,$$

$\boldsymbol{\rho}_{01}=(\mathbf{r}_{21},\mathbf{r}_{31})$, and D is the ball $\rho_{01}\leqslant r_0$. By employing the six-dimensional Wigner transformation $\mathscr{W}$, we can transform

$$\frac{i}{\hbar}\int_D d\rho_{01}\left[\sum_{\mu\nu}M_{\mu\nu}{}^{-1}\hat{\mathbf{P}}_{\mu1}\hat{\mathbf{P}}_{\nu1},\hat{G}_4\right]_{\rho_{01}'=\rho_{01}}$$
$$=\int_\sigma d\sigma\sum_{\mu\nu}\frac{\mathbf{r}_{\mu1}}{\rho_{01}}M_{\mu\nu}{}^{-1}[\hat{\mathbf{P}}_{\nu1},\hat{G}_4]_+|_{\rho_{01}'=\rho_{01}}$$

into

$$2\int_\sigma d\sigma\int d\mathbf{P}_{21}\,d\mathbf{P}_{31}\sum_{\mu\nu}\frac{\mathbf{r}_{\mu1}}{\rho_{01}}M_{\mu\nu}{}^{-1}\mathbf{P}_{\nu1}\mathscr{W}[\hat{G}_4]$$
$$=2\int_\sigma d\sigma\int d\mathbf{P}_{21}\,d\mathbf{P}_{31}\left(\frac{\mathbf{r}_{21}}{\rho_{01}}\mathbf{v}_{21}+\frac{\mathbf{r}_{31}}{\rho_{01}}\mathbf{v}_{31}\right)\mathscr{W}[\hat{G}_4].$$

In all other respects the generalization of the proof in Sec. 3 to the case of the A + B + C⇄D reactions requires no special comment.

APPENDIX A. SUBSTANTIATION OF EQ. (2.11)

We will focus our attention on the dependence of various functions $\mathbf{r}_{12}$, $\mathbf{r}_{12}'$, and $\mathbf{P}_{12}$. The other variables $\mathbf{P}_3$, q_1, q_2, q_1', and q_2' are at first considered fixed and will not be written out explicitly. Consider the Wigner transformation

$$F(\mathbf{r}_{12},\mathbf{P}_{12})=\mathscr{W}_0[\hat{f}_3]=(2\pi\hbar)^{-3}\mathscr{V}_0[\hat{f}_3],\tag{A1}$$

where $\mathscr{V}_0$ stands for the Weyl transformation

$$\mathscr{V}_0[\hat{f}_3]=\int\exp(-i\hbar^{-1}\mathbf{P}_{12}\mathbf{s})f_3\left(\mathbf{r}_{12}+\frac{\mathbf{s}}{2},\mathbf{r}_{12}-\frac{\mathbf{s}}{2}\right)ds.\tag{A2}$$

If we introduce the function $u(\mathbf{r},\mathbf{s})$ via the equality

$$f_3(\mathbf{r}_{12},\mathbf{r}_{12}')=u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}'\right)$$

then

$$F(\mathbf{r}_{12},\mathbf{P}_{12})=(2\pi\hbar)^{-3}\int\exp(-i\hbar^{-1}\mathbf{P}_{12}\mathbf{s})u(\mathbf{r}_{12},\mathbf{s})\,ds.$$

Differentiating the inverse transformation

$$u(\mathbf{r}_{12},\mathbf{s})=\int\exp(i\hbar^{-1}\mathbf{P}_{12}\mathbf{s})F(\mathbf{r}_{12},\mathbf{P}_{12})d\mathbf{P}_{12},\tag{A3}$$

we obtain

$$-[u(\mathbf{r}_{12},0)]^{-1}\nabla_s{}^2u(\mathbf{r}_{12},\mathbf{s})|_{s=0}$$
$$=\hbar^{-2}\left[\int F(\mathbf{r}_{12},\mathbf{P}_{12})d\mathbf{P}_{12}\right]^{-1}\int P_{12}{}^2F(\mathbf{r}_{12},\mathbf{P}_{12})d\mathbf{P}_{12}.$$

The right-hand side of this equality can be estimated in order of magnitude at $(\Delta P/\hbar)^2$. This suggests that the function $u(\mathbf{r}_{12},\mathbf{s})$ varies rapidly with $\mathbf{s}$; specifically, its characteristic scale (the distance over which it changes significantly) is $\hbar/\Delta P$. Let us assume that the dependence of $u(\mathbf{r}_{12},\mathbf{s})$ on $\mathbf{s}$ is characterized by a single scale factor. If $F(0,\mathbf{P}_{12})$ is differentiable a sufficient number of times, its Fourier transform $u(0,\mathbf{s})$ decreases sufficiently rapidly as $|\mathbf{s}|$ grows, and for large values of $|\mathbf{s}|$ the following asymptotic formula holds true: $|u(0,\mathbf{s})|\approx C|\mathbf{s}|^{-k}$, $k\geqslant1$. Determining the constant C from dimensional considerations, we obtain for $|\mathbf{s}|\gg\hbar/\Delta P$

$$|u(0,\mathbf{s})|\sim|u(0,\mathbf{s})|_{s\sim\hbar/\Delta P}(\hbar/\Delta P)^k|\mathbf{s}|^{-k}.$$

If $F(\mathbf{r}_{12},\mathbf{P}_{12})$ is differentiable in P_{12}, a similar formula exists for every $r_{12}\sim r_0$:

$$|u(\mathbf{r}_{12},\mathbf{s})|\sim|u(\mathbf{r}_{12},\mathbf{s})|_{s\sim\hbar/\Delta P}(\hbar/\Delta P)^k|\mathbf{s}|^{-k}.\quad|\mathbf{s}|\gg\hbar/\Delta P,\tag{A4}$$

where the fact that the dependence of $u(\mathbf{r}_{12},\mathbf{s})$ on $\mathbf{s}$ is characterized by a single constant $\hbar/\Delta P$ was employed. We have

$$|\mathbf{s}u(\mathbf{r}_{12},\mathbf{s})|\leqslant(\hbar/\Delta P)|u(\mathbf{r}_{12},\mathbf{s})|_{s\sim\hbar/\Delta P}.\tag{A5}$$

The validity of this formula for $|\mathbf{s}|\sim\hbar/\Delta P$ and $|\mathbf{s}|\ll\hbar/\Delta P$ is obvious and for $|\mathbf{s}|\gg\hbar/\Delta P$ follows from (A4).

Now let us examine the behavior of u as a function of $\mathbf{r}_{12}$. In a region L where $r_{\text{int}}\ll r_{12}\sim r_0$, molecules A and B do not interact; their motion is purely kinematic. From the validity of the equation

$$\dot{\hat{f}}_3=-(i/\hbar)(2M_0)^{-1}[\hat{P}_{12}{}^2,\hat{f}_3],$$

assuming that $\mathbf{r}_{12}'=\mathbf{r}_{12}'$, and employing (2.9) we easily find that

$$\frac{\partial}{\partial t}\int F\,d\mathbf{P}_{12}=-\frac{1}{M_0}\nabla_{12}\int\mathbf{P}_{12}F\,d\mathbf{P}_{12}$$

or $\dot{n}=-\nabla_{12}(\langle\mathbf{v}_{12}\rangle n)$, where $n=\int F(\mathbf{r}_{12},\mathbf{P}_{12})d\mathbf{P}_{12}$ is the spatial density, and $\langle\mathbf{v}_{12}\rangle=(M_0n)^{-1}\int\mathbf{P}_{12}Fd\mathbf{P}_{12}$ the mean velocity. In usual conditions, n and F are changing with time quite slowly, i.e., $t\sim n/|\dot{n}|$ time of the change is much longer than the $\tau_n\sim r_n/|\langle\mathbf{v}_{12}\rangle|$, $\tau_v\sim r_v/\langle\mathbf{v}_{12}\rangle|$ time of flight, where $r_n\sim n/|\nabla_{12}n|$, $r_v\sim|\langle\mathbf{v}_{12}\rangle|/\nabla_{12}\langle\mathbf{v}_{12}\rangle|$. From $\tau\gg\tau_n$, $\tau\gg\tau_v$ follows that the $\dot{n}$ derivative can be ignored compared with $\langle\mathbf{v}_{12}\rangle\nabla_{12}n$ and $n\nabla_{12}\langle\mathbf{v}_{12}\rangle$.
Then

$$\nabla_{12}(\langle\mathbf{v}_{12}\rangle n)\approx0.$$

This yields

$$|\nabla_{12}n|/n\sim|\nabla_{12}\langle\mathbf{v}_{12}\rangle|/|\langle\mathbf{v}_{12}\rangle|.\tag{A6}$$

The mean velocity consists of two parts, $\langle\mathbf{v}_{12}\rangle=\mathbf{a}+\mathbf{b}$, where $\mathbf{a}$ is the velocity $\mathbf{v}_{12}$ averged over molecules A and B not interacting with each other (this part is independent of $\mathbf{r}_{12}$), and $\mathbf{b}$ is the velocity averaged over molecules A and B formed as a result of dissociation of C. Such molecules emerge in region L_0, which is much smaller than L. In L we can put $\mathbf{b}\approx\varphi(\mathbf{l})\mathbf{l}$, with $\mathbf{l}=\mathbf{r}_{12}/r_{12}$. This corresponds to motion from L_0, which is assumed to be practically a point, with $\varphi > 0$ a function. The result is

$$|\nabla_{12}\mathbf{b}|/|\mathbf{b}| \sim 1/r_0 + |\nabla_l\varphi|/(r_0\varphi).$$

In the case of quantum diffraction we have $|\nabla_l\varphi|/\varphi \lesssim r_{\rm int}\Delta P/\hbar$. Combining this with (A6), we obtain

$$|\nabla_{12}n|/n \leqslant 1/r_0 + r_{\rm int}\Delta P/(\hbar r_0).$$

Since $n = u(\mathbf{r}_{12},0)$ owing to (A3), we can write the above relation as

$$|\nabla_{12}u(\mathbf{r}_{12},0)|/u(\mathbf{r}_{12},0) \leqslant 1/r_0 + r_{\rm int}\Delta P/(\hbar r_0).$$

If the dependence of $u(\mathbf{r}_{12},\mathbf{s})$ on $\mathbf{r}_{12}$ is characterized in L by a single scaling distance, we have

$$|\nabla_{12}u(\mathbf{r}_{12},\mathbf{s})|/|u(\mathbf{r}_{12},\mathbf{s})| \leqslant 1/r_0 + r_{\rm int}\Delta P/(\hbar r_0). \tag{A7}$$

Let us now consider the matrix product

$$[\hat f_3^{(2)}]_{\mathbf{r}_{12},\mathbf{r}_{12}'} \equiv [\hat f_3\hat f_3]_{\mathbf{r}_{12},\mathbf{r}_{12}'} = \int f_3(\mathbf{r}_{12},\mathbf{r}_{12}'')f_3(\mathbf{r}_{12}'',\mathbf{r}_{12}')\,d\mathbf{r}_{12}''$$
$$= \int u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}''}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right)u\left(\frac{\mathbf{r}_{12}''+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}''-\mathbf{r}_{12}'\right)d\mathbf{r}_{12}''. \tag{A8}$$

Here we have written $\hat f_3^{(2)}$ instead of $\hat f_3^2$ because the other variables q_1, q_2, q_1', and q_2' in the various factors may have different values. We take the Taylor expansion

$$u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}''}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right) = u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right) + \frac{\mathbf{r}_{12}''-\mathbf{r}_{12}'}{2}\nabla_1 u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right) + \ldots,$$

where ∇_1 is the del operator referring to the first vector argument of u, and higher-order terms have not been written. In view of the last equality we have

$$u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}''}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right)u\left(\frac{\mathbf{r}_{12}''+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}''-\mathbf{r}_{12}'\right)$$
$$= u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right)u\left(\frac{\mathbf{r}_{12}''+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}''-\mathbf{r}_{12}'\right) + T,$$

where

$$T = \nabla_1 u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}'\right)\mathbf{v} + \ldots,$$
$$\mathbf{v} = \frac{\mathbf{r}_{12}''-\mathbf{r}_{12}'}{2}u\left(\frac{\mathbf{r}_{12}''+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}''-\mathbf{r}_{12}'\right).$$

Because of (A5) we can obtain the estimate:

$$|\mathbf{v}| \leqslant \frac{\hbar}{\Delta P}|u|_{s\sim\hbar/\Delta P} \qquad \text{for every} \qquad \mathbf{r}_{12}'',$$

and in view of (A7) we have

$$|T| \leqslant \left(\frac{\hbar}{r_0\Delta P} + \frac{r_{B3}}{r_0}\right)|uu|_{s\sim\hbar/\Delta P} \quad \text{for} \quad \frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2} \in L.$$

Hence, the correction T is fairly small for $r_0\Delta P \gg \hbar$ and $r_0 \gg r_{\rm int}$ and the contribution in the integration with respect to $\mathbf{r}_{12}$ is small. We can prove in a similar manner that in the integral in (A8) we can replace $u((\mathbf{r}_{12}''+\mathbf{r}_{12}')/2,\mathbf{r}_{12}''-\mathbf{r}_{12}'))$ with $u((\mathbf{r}_{12}+\mathbf{r}_{12}')/2,\mathbf{r}_{12}''-\mathbf{r}_{12}')$ and obtain

$$[\hat f_3^{(2)}]_{\mathbf{r}_{12},\mathbf{r}_{12}'} \approx \int u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}''\right)u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}''-\mathbf{r}_{12}'\right)d\mathbf{r}_{12}''$$

for $(\mathbf{r}_{12}+\mathbf{r}_{12}')/2 \in L$. Applying the Weyl transformation (A2) to both sides of this equality, we find that

$$\mathscr{V}_0[\hat f_3^{(2)}] \approx F(\mathbf{r}_{12},\mathbf{P}_{12})F(\mathbf{r}_{12},\mathbf{P}_{12}) \equiv \{\mathscr{V}_0[\hat f_3]\}^{(2)}, \quad r_{12} \gg r_{\rm int}.$$

What is important is that $\tilde u$, defined as

$$[\hat f_3^{(2)}]_{\mathbf{r}_{12},\mathbf{r}_{12}'} = \tilde u\left(\frac{\mathbf{r}_{12}+\mathbf{r}_{12}'}{2},\mathbf{r}_{12}-\mathbf{r}_{12}'\right),$$

has the same properties (A5) and (A7) as the function u. This means that by using the same method we can obtain

$$\mathscr{V}_0[\hat f_3^{(3)}] \approx \{\mathscr{V}_0[\hat f_3]\}^{(3)}, \quad r_{12} \gg r_{\rm int}.$$

By mathematical induction,

$$\mathscr{V}_0[\hat f_3^{(n)}] \approx \{\mathscr{V}_0[\hat f_3]\}^{(n)}, \quad r_{12} \gg r_{\rm int}. \tag{A9}$$

We now lift the restriction that the variables q_1, q_2, q_1' and q_2' must be fixed in each factor and consider the matrices $\mathscr{V}_0[\hat f_3]$ and $\hat f_3$ in these variables and the powers of these matrices.

Then instead of (A9) we have

$$\mathscr{V}_0[\hat f_3^n] \approx \{\mathscr{V}_0[\hat f_3]\}^n, \quad r_{12} \gg r_{\rm int}. \tag{A10}$$

Employing the expansion

$$\ln(\gamma_3\hat f_3) = \ln(\hat I + \gamma_3\hat f_3 - \hat I) = \sum_{k=1}^{\infty}\frac{(-1)^{k-1}}{k}(\gamma_3\hat f_3 - \hat I)^k$$

and allowing for (A10), where instead of $\hat f_3$ we have taken $\gamma_3\hat f_3 - \hat I$, we find that

$$\mathscr{V}_0[\hat f_3\ln(\gamma_3\hat f_3)] \approx \mathscr{V}_0[\hat f_3]\ln\{\gamma_3\mathscr{V}_0[\hat f_3]\}, \quad r_{12} \gg r_{\rm int}$$

or the sought formula (2.11) if we allow for the fact that $\mathscr{W}_0[\hat A] = (2\pi\hbar)^{-3}\mathscr{V}_0[\hat A]$, according to (A1).

APPENDIX B. PROOF OF INEQUALITY (3.12)

Let us first prove that for any two Hermitian operators $\hat A$ and $\hat D$ the following inequality holds true:

$$\operatorname{Tr}\hat A\hat D \leqslant \max_P \sum_i \lambda_i\mu_{j(i)}, \tag{B1}$$

where λ_i and μ_j are the eigenvalues of matrices $\hat A$ and $\hat D$, respectively. Minimization on the right-hand side of Eq. (B1) is carried out over all permutations $j(i)$. Indeed, in the $\hat A$-representation, $\operatorname{Tr}\hat A\hat B$ can be written as $\Sigma\lambda_i D_{ii}$, with

$$D_{ik} = \sum_j u_{ij}\mu_j(u^+)_{jk} = \sum_j u_{ij}\mu_j u_{kj}^*,$$

so that

$$D_{ii} = \sum_j |u_{ij}|^2\mu_j,$$

where u_{ij} is the unitary matrix of the transformation from the $\hat D$-representation to the $\hat A$-representation. Hence, inequality

(B1) can be transformed into the following form:

$$\lambda^T \hat{H} \mu \leqslant \max_{\alpha} \lambda^T \hat{M}_\alpha \mu, \tag{B2}$$

where μ is the column matrix constructed from the μ_j eigenvalues, $\lambda^T$the row matrix constructed from the λ_i eigenvalues, $\hat{H}$ a matrix whose elements are $|u_{ij}|^2$, and $\hat{\mathbf{M}}_\alpha$ the permutation matrix, whose elements are either zero or unity. The $\hat{H}$ matrix, in view of the property that $\hat{U}\hat{U}^+ = \hat{I}$, is bistochastic (i.e, has nonnegative elements and the sum of the elements of each row and column is equal to unity) and moreover orthostochastic. According to Birkhoff's theorem (see, e.g., Ref. 6), every bistochastic matrix can be written in the form of the following sum:

$$H = \sum_{\alpha} p_\alpha \hat{M}_\alpha, \tag{B3}$$

where the coefficients p_α are nonnegative and such that $\Sigma p_\alpha = 1$. Substituting (B3) into (B2), we obtain an equivalent inequality,

$$\sum_{\alpha} p_\alpha (\bar{a} - a_\alpha) \geqslant 0$$

($a_\alpha = \lambda^T \hat{M}_\alpha \mu$ and $\bar{a} = \max a_\alpha$), whose validity is obvious because all the p_α and $\bar{a} - a_\alpha$ are nonnegative. This completes the proof of inequality (B1).

Let us now turn to the proof of inequality (3.12). We put $\hat{D} = \ln \hat{B}$. Then the eigenvalues b_j of matrix $\hat{B}$ are related to the μ_j through the equalities $\mu_j = \ln b_j$. Matrix $\hat{D}$ is Hermitian if $\hat{B}$ is Hermitian and positive definite. Taking the permutation $j(i)$ at which the sum $\Sigma_i \Lambda_i \mu_{j(i)}$ assumes its maximum value, we find that (B1) yields

$$-\mathrm{Tr}\, \hat{A} \ln \hat{B} \geqslant -\sum_i \lambda_i \ln b_{j(i)}. \tag{B4}$$

Adding (B4) to the obvious equalities

$$\mathrm{Tr}\, \hat{B} = \sum_j b_j = \sum_i b_{j(i)}, \quad \mathrm{Tr}(\hat{A} \ln \hat{A} - \hat{A}) = \sum_i \lambda_i (\ln \lambda_i - 1),$$

we arrive at

$$\mathrm{Tr}[\hat{A} \ln \hat{A} - \hat{A} + \hat{B} - \hat{A} \ln \hat{B}] \geqslant \sum_i [\lambda_i \ln \lambda_i - \lambda_i + b_{j(i)} - \lambda_i \ln b_{j(i)}]. \tag{B5}$$

The expression within the brackets on the right-hand side is nonnegative for every value of i since it is equal to $\lambda_i F(b_{j(i)} / \lambda_i)$, where $F(y) = y - 1 - \ln y$ is a non-negative function and the λ_i are nonnegative because matrix $\hat{A}$ is nonnegative definite. The fact that the right-hand side of (B5) is nonnegative proves the validity of (3.12)

Strictly speaking, the above proof is valid only for matrices of finite rank. However, by enforcing a special limiting process in which the volume of the space tends to infinity and the discreteness step to zero it is possible to extend these inequalities to a more general case.

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